

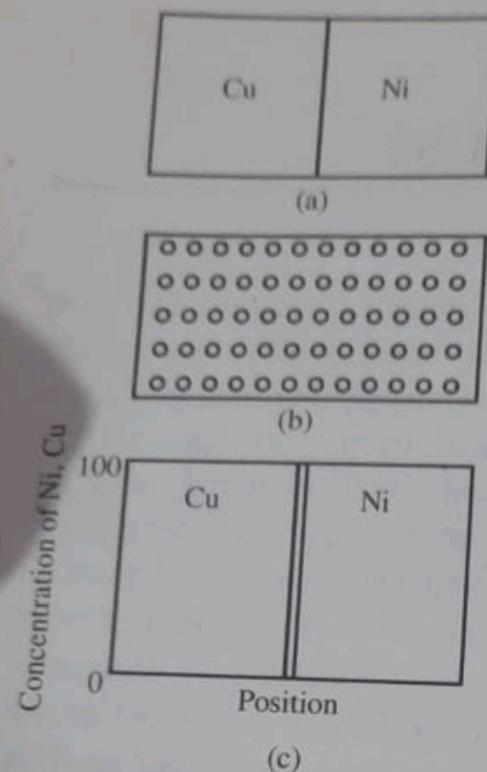
## CHAPTER 5

# DIFFUSION IN SOLIDS

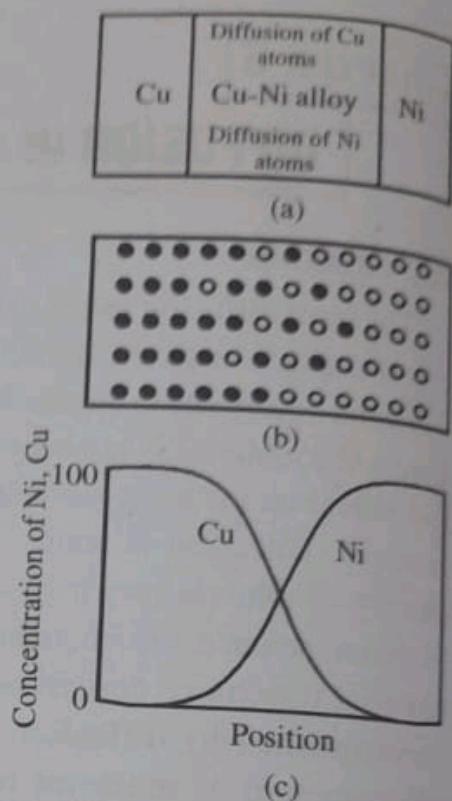
### Introduction

The term diffusion refers to the movement of atoms. Diffusion can take place in gases, liquids and solids. In solids, particularly diffusion occurs due to thermally activated random motion of atoms unless the material is at absolute zero temperature (zero kelvin), individual atoms keep vibrating and eventually move within the material. Diffusion in solids is a very slow process because the density of solids is very high as compared to liquids and gases. In materials science it is frequently necessitates the addition of other material to achieve desired properties. **This transfer of mass is accomplished by diffusion. Thus diffusion is defined as the phenomenon of material transport by atomic motion.** This chapter deals with the atomic mechanisms by which diffusion occurs, the mathematics of diffusion and the diffusing species on the rate of diffusion.

The phenomenon of diffusion may be demonstrated by taking two metals say copper and nickel. These two metal bars are joined together to have intimate contact between the two faces as shown in figure 5.1 (a). The combined system is called a diffusion couple. This couple is heated for a long period at a high temperature below the melting point of both and cool to room temperature. chemical analysis shows that pure copper and nickel are found at the extreme ends separated by an alloy region. Concentration of both metals found to vary with position. It is depicted in figure 5.2.



**Figure 5.1:** (a) A copper-nickel diffusion couple before a high-temperature heat treatment (b) Schematic representations of Cu (closed circles) and Ni (open circles) atom locations within the diffusion couple (c) Concentrations and nickel as a function of position across couple.



**Figure 5.2:** (a) A copper-nickel diffusion couple after a high-temperature heat treatment, showing the alloyed diffusion zone, (b) Schematic representations of Cu (closed circles) and Ni (open circles) atom locations within the couple, (c) Concentrations of copper and nickel as a function of position across the couple.

This implies that copper atoms have migrated or diffused into nickel and vice-versa. This process is called interdiffusion or impurity diffusion. Diffusion also occurs for a single crystal where atoms exchange their positions. This is termed as selfdiffusion.

### Diffusion mechanisms

From atomic point of view, diffusion is the migration of atoms from lattice site to lattice site. Actually atoms in solid materials

are in constant motion i.e., rapidly changing positions. For an atom to make such a move, two conditions are to be satisfied. **They are 1) there must be an empty adjacent site and 2) the atom must have sufficient energy to break bonds with its neighbour atoms and then cause some lattice distortion during the displacement.** This energy is vibration in nature. At a specific temperature a small fraction of the total number of atoms is capable of diffusion due to its vibrational energy. This fraction increases with increasing temperature.

Several different models for this have been proposed. Here we discuss only two of them. They are :

- 1) vacancy diffusion and 2) interstitial diffusion.

### Vacancy diffusion

**Vacancy diffusion is a process by which an atom from a lattice site move to an adjacent vacancy site.**

For this process to occur there must exist vacancies. Vacancies are due to defects. Thus vacancy diffusion is a function of number of vacancies available. We know that large number of vacancies are present when the metal is heated when an atom moves from a site to a vacancy, a vacancy is produced at the former position of the atom. In other words we can say that vacancies change their

Motion of a host or substitutional atom

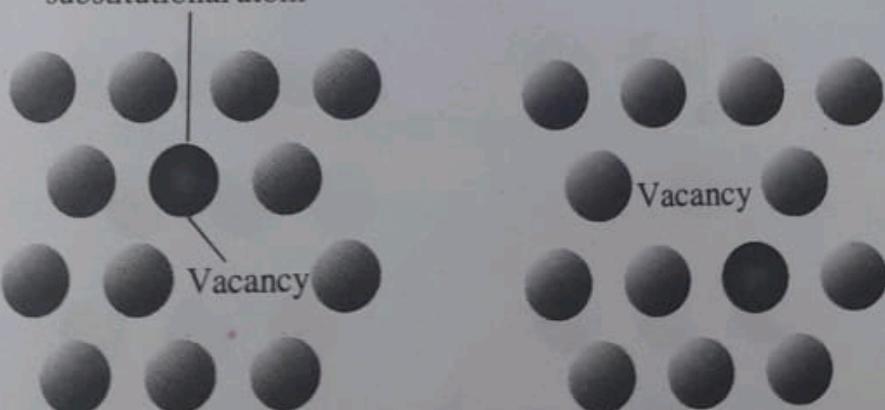


Figure 5.3: Schematic representations of vacancy diffusion

positions. Diffusion of atoms in direction corresponds to the motion of vacancies in the opposite direction. Diffusion may occur in the same metal known as self diffusion, for this impurity atom must be substituted for host atoms. Atoms of one metal can also move to another metal kept in contact. This is known as interdiffusion process. This is depicted in figure 5.3.

### Interstitial diffusion

Interstitial diffusion is a process by which an atom migrates from one interstitial position to a neighbouring interstitial position that is vacant.

This type of mechanism is found for interdiffusion of impurities such as hydrogen, carbon, nitrogen, oxygen etc. This is because these atoms are small enough to fit into the interstitial positions. Substitutional impurity atoms, creating self diffusion, rarely go for interstitial diffusion.

In most metal alloys interstitial diffusion occurs much faster than vacancy diffusion since interstitial atoms are smaller and thus more mobile. i.e., the probability of occurrence of interstitial diffusion is more comparing to vacancy diffusion.

The schematic representation of interstitial diffusion is depicted in figure 5.4.

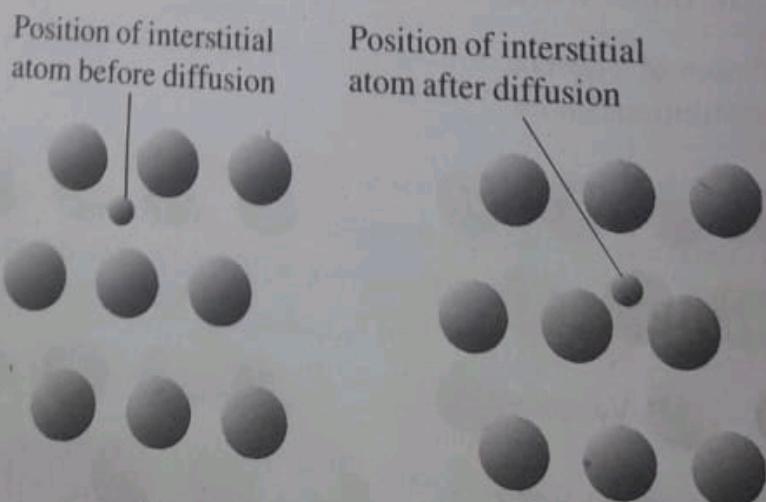


Figure 5.4: Interstitial diffusion

### Steady state diffusion

We found that diffusion is a process of transfer of atoms. In a macroscopic sense it is a transfer of mass. Hence diffusion is a time dependent process. So often it needs to know the rate of mass transfer. This is usually expressed as diffusion flux ( $J$ ). It is defined as the mass ( $M$ ) or number of atoms diffusing through unit area perpendicular to the surface in unit time.

$$\text{i.e., } J = \frac{M}{At} \quad \dots \dots (1)$$

Where  $M$  is the mass that diffuses in time  $t$  through an area  $A$ .

In differential form equation (1) can be put in the form.

$$J = \frac{1}{A} \frac{dM}{dt} \quad \dots \dots (2)$$

Its unit is  $\text{kgm}^{-2}\text{s}^{-1}$  or atoms  $\text{m}^{-2}\text{s}^{-1}$ .

If the diffusion flux does not change with time it is known as steady state physically the steady state condition is attained when the concentration of the diffusing species on both sides of an alloy are held constant.

If  $C_1$  and  $C_2$  are the concentrations at positions  $x_1$  and  $x_2$  respectively, then the concentration gradient

$$= \frac{C_1 - C_2}{x_1 - x_2}$$

In differential form concentration gradient =  $\frac{dC}{dx}$

Thus diffusion flux

$$J \propto \frac{dC}{dx}$$

or

$$J = D \frac{dC}{dx}$$

Where D is called diffusion coefficient.

In the above expression there is a mathematical inconsistency. On the L.H.S diffusion takes from higher concentration to lower concentration (decreasing), but on the L.H.S  $\frac{dC}{dx}$  is increasing, since the derivative is positive. So to make the equation mathematically consistent we put a negative sign.

$$\text{Thus } J = -D \frac{dC}{dx} \quad \dots \dots (3)$$

The unit of D is  $m^2 s^{-1}$ . Equation (2) is called Fick's first law.

### Nonsteady state diffusion

If the diffusion flux  $D \frac{dC}{dx}$  changes with position and the

concentration gradient changes with time, diffusion is said to be non-steady state. Thus the governing equation is a partial differential equation as C is a function of x and t.

$$\frac{dC}{dt} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)$$

or

$$\frac{dC}{dt} = D \frac{\partial^2 C}{\partial x^2} \quad \dots \dots (4)$$

It is known as Fick's second law.

A physically meaningful solution to the partial differential will be obtained by specifying the appropriate conditions (two). The solution to eq (4) is found to be

$$C(x, t) = A - B \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \quad \dots \dots (5)$$

where  $\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$  is called the Gaussian error function. This function is defined as

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy$$

At  $x = 0$ ,  $\text{erf}(0) = 0$

At  $x = \infty$

$$\text{erf}(\infty) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-y^2} dy$$

$$= \frac{2}{\sqrt{\pi}} \frac{\sqrt{\pi}}{2} = 1$$

At  $x = -\infty$

$$\text{erf}(-\infty) = \frac{2}{\sqrt{\pi}} \int_0^{-\infty} e^{-y^2} dy = -1$$

where  $\int_0^{\infty} e^{-y^2} dy = \frac{\sqrt{\pi}}{2}$  is used (see example 3).

While solving the partial differential equation (4), the following assumptions are made

1. Before diffusion, diffusing solute atoms in the solid atoms are uniformly distributed with concentration  $C_0$ .
2. The value of  $x$  at the surface is zero and increases with distance into the solid.
3. The time is taken to be zero the instant before the diffusion process begins. These boundary conditions are stated as

For  $t = 0$ ,  $C = C_0 \quad 0 \leq x \leq \infty$

For  $t > 0$ ,  $C = C_s \quad \text{at } x = 0$

$C_s$  is the constant surface concentration

and  $C = C_0$  at  $x = \infty$ .

Now we can apply these conditions to the solution eq (5),

For  $t = 0$ ,  $C = C_0$ , eq (5) gives

$$C(x, 0) = C_0 = A - B \operatorname{erf}(\infty)$$

$$\therefore C_0 = A - B$$

..... (6)

For  $t > 0$ ,  $C = C_s$  at  $x = 0$ , eq (5) gives

$$C(0, t) = C_s = A - B \operatorname{erf}(0)$$

$$C_s = A$$

$$(\because \operatorname{erf}(0) = 0)$$

..... (7)

$$\therefore C(x, t) - C_0 = A - B \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) - (A - B)$$

$$C(x, t) - C_0 = B - B \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$C(x, t) - C_0 = B \left(1 - \operatorname{erf}\frac{x}{2\sqrt{Dt}}\right)$$

or

$$\frac{C(x, t) - C_0}{B} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x, t) - C_0}{A + B - A} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\frac{C(x, t) - C_0}{A - (A - B)} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \quad \dots \dots (8)$$

This gives the solution. Knowing  $C_0$  and  $C_s$ ,  $C(x, t)$  is the concentration at depth  $x$  after a time  $t$  can be calculated.

**Note:** Error function values can be taken from error function tables.

If we want to evaluate the specific concentration of a salute say

$$C(x, t) = C_1$$

then  $\frac{C_1 - C_0}{C_s - C_0}$  the L.H.S of eq (8) becomes a constant so R.H.S

should also be a constant.

$$\text{i.e., } \frac{x}{2\sqrt{Dt}} = \text{constant}$$

$$\text{or } \frac{x^2}{Dt} = \text{constant} \quad \dots \dots (9)$$

Usually an alloy say iron-carbon has a uniform carbon concentration. For some applications, it is necessary to harden the surface of alloy. This can be accomplished by increasing the surface concentration. This process is called carburization. For this alloy is exposed at an elevated temperature to an atmosphere rich in a hydrocarbon gas such as methane  $\text{CH}_4$ . The time of exposition can be calculated by using eq (8). see example 1.

**Note:** The boundary condition stated above where the surface concentration is held constant is well suited for semi-infinite solid. A bar of solid is considered to be semi-solid

if none of the diffusing atoms reaches the bar end during the time over which diffusion takes place.

### Example 1

An alloy (iron-carbon) has a uniform concentration of 0.25 mass% and is to be treated at 950°C. If the concentration of carbon at the surface is suddenly brought to and maintained at 1.20 mass%, how long will it take to achieve a carbon content of 0.80 mass% at a position 0.5mm below the surface.  $D = 1.6 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ . The error function  $z$  corresponding to 0.4210 is 0.392.

### Solution

$$\left. \begin{array}{l} C_0 = 0.25 \text{ mass\% of C} \\ C_s = 1.20 \text{ mass\% of C} \\ C(x, t) = 0.80 \text{ mass\% of C} \\ x = 5 \times 10^{-4} \text{ m} \\ D = 1.6 \times 10^{-11} \text{ m}^2 \text{s}^{-1} \\ t = ? \end{array} \right\} \text{given}$$

From eq (8), we have

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{D}{2\sqrt{Dt}}\right)$$

Substituting all the values, we get

$$\frac{0.8 - 0.25}{1.2 - 0.25} = 1 - \operatorname{erf}\left(\frac{5 \times 10^{-4}}{2\sqrt{1.6 \times 10^{-11} t}}\right)$$

$$L.H.S = \frac{0.55}{0.95} = 0.579$$

$$0.579 = 1 - \operatorname{erf}\left(\frac{5 \times 10^{-4}}{2\sqrt{1.6 \times 10^{-11} t}}\right)$$

$$\operatorname{erf}\left(\frac{5 \times 10^{-4}}{2\sqrt{1.6 \times 10^{-11} t}}\right) = 1 - 0.579 = 0.421$$

$$\operatorname{erf}\left(\frac{62.5}{t^{\frac{1}{2}}}\right) = 0.421$$

$$\operatorname{erf}\left(\frac{62.5}{t^{\frac{1}{2}}}\right) = \operatorname{erf}(0.392) \text{ gives}$$

$$\frac{62.5}{t^{\frac{1}{2}}} = 0.392$$

$$t = \left(\frac{62.5}{0.392}\right)^2 = 24520.72 \text{ s}$$

$$t = \frac{24520.72}{60 \times 60} \text{ hours}$$

$$t = 7.06 \text{ hours}$$

**Note :** Usually error function is calculated from error function tables.

### Example 2

The diffusion coefficients for copper in aluminium at 500 and 600°C are  $4.8 \times 10^{-14}$  and  $5.3 \times 10^{-13} \text{ m}^2 \text{s}^{-1}$  respectively. Determine the approximate time at 500°C that will produce the same diffusion result as a 10 hour heat treatment at 600°C.

### Solution

We know that while achieving specific concentration of solute,

$\frac{x}{2\sqrt{Dt}}$  is a constant.

$$\text{i.e., } \frac{x_1}{2\sqrt{D_1 t_1}} = \frac{x_2}{2\sqrt{D_2 t_2}}$$

But  $x_1 = x_2$  given

$$\therefore D_1 t_1 = D_2 t_2$$

$$D_{500} t_{500} = D_{600} t_{600}$$

$$\text{or } t_{500} = \frac{D_{600} t_{600}}{D_{500}}$$

$$t_{500} = \frac{5.3 \times 10^{-13} \times 10}{4.8 \times 10^{-14}} = 110.4 \text{ h.}$$

### Example 3

Show that  $\text{erf}(\infty) = 1$

#### Solution

By definition

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

$$\therefore \text{erf}(\infty) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-y^2} dy$$

$$\text{Let } I = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-y^2} dy \quad \dots\dots (1)$$

$$\text{or } I = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-x^2} dx \quad \dots\dots (2)$$

Eq (1) × Eq (3) gives

$$I^2 = \frac{4}{\pi} \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx dy$$

Put  $x = r \cos \theta$ ,  $y = r \sin \theta$

$$x^2 + y^2 = r^2$$

and  $dx dy = r dr d\theta$ .

Here  $r$  goes from 0 to  $\infty$  and  $\theta$  goes from 0 to  $\pi/2$ .  
Hence

$$I^2 = \frac{4}{\pi} \int_0^{\infty} \int_0^{\pi/2} e^{-r^2} r dr d\theta$$

$$I^2 = \frac{4}{\pi} \int_0^{\pi/2} d\theta \int_0^{\infty} e^{-r^2} r dr$$

$$I^2 = \frac{4}{\pi} \cdot \frac{\pi}{2} \int_0^{\infty} e^{-r^2} r dr$$

$$I^2 = 2 \int_0^{\infty} e^{-r^2} r dr$$

Put  $r^2 = t$ , then  $2r dr = dt$

.....(1)

$$I^2 = 2 \int_0^{\infty} e^{-t} \frac{dt}{2} = \int_0^{\infty} e^{-t} dt$$

.....(2)

$$I^2 = [-e^{-t}]_0^{\infty} = [-e^{-\infty} - -e^0]$$

$$I^2 = 0 + 1 = 1$$

$$\therefore I = 1$$

$$\text{i.e., } \operatorname{erf}(\infty) = 1$$

### Example 4

From the given error function table, evaluate z corresponding to  $\operatorname{erf} 0.421$ .

| <u>z</u> | <u><math>\operatorname{erf}(z)</math></u> |
|----------|---|
| 0.35     | 0.3794                                    |
| <u>z</u> | <u>0.4210</u>                             |
| 0.40     | 0.4284                                    |

### Solution

From the given table, we have

$$\frac{z - 0.35}{0.40 - 0.35} = \frac{0.4210 - 0.3794}{0.4284 - 0.3794}$$

$$\frac{z - 0.35}{0.05} = \frac{0.0416}{0.049}$$

$$z - 0.35 = 0.8489 \times 0.05$$

$$z - 0.35 = 0.42445$$

$$\therefore z = 0.392$$

### Factors that influence diffusion

In diffusion process (steady state as well as non-steady state) the diffusion coefficient plays a major role because it is an indication of the rate at which diffusion takes place. There are two factors which influence diffusion coefficient. They are 1) species and 2) temperature. The diffusing species as well as host materials influence  $D$ . It is found that there is significant difference in magnitude between self diffusion and interstitial diffusion.

Another influencing factor is temperature. When temperature is increased diffusion coefficient is found to increase.

The temperature dependence of the diffusion coefficient is given by

$$D = D_0 e^{\frac{-E_d}{RT}} \quad \dots \dots (10)$$

Where  $D_0$  is the diffusion coefficient at 0K,  $E_d$  is the activation energy for diffusion, R is the universal gas constant and T is the temperature in kelvin.

**Activation energy is defined as the energy required to produce the diffusion motion of one mole of atoms.** It is measured in J/mol or eV/atom.

A table of diffusion data ( $D_0$  and D) at various temperatures for different metals are given below.

Table 5.1 Diffusion Data

| Host Metal             | $D_0(m^2/s)$         | Activation Energy $E_d$ |         | Calculated Values |                       |
|------------------------|----------------------|-------------------------|---------|-------------------|-----------------------|
|                        |                      | kJ/mol                  | eV/atom | T( $^{\circ}$ C)  | $D(m^2/s)$            |
| $\alpha$ -Fe<br>(BCC)  | $2.8 \times 10^{-4}$ | 251                     | 2.60    | 500               | $3.0 \times 10^{-21}$ |
|                        |                      |                         |         | 900               | $1.8 \times 10^{-15}$ |
| $\gamma$ - Fe<br>(FCC) | $6.0 \times 10^{-5}$ | 284                     | 2.94    | 900               | $1.1 \times 10^{-17}$ |
|                        |                      |                         |         | 1100              | $7.8 \times 10^{-16}$ |
| $\alpha$ -Fe           | $6.2 \times 10^{-7}$ | 80                      | 0.83    | 500               | $2.4 \times 10^{-12}$ |
|                        |                      |                         |         | 900               | $1.7 \times 10^{-10}$ |
| $\gamma$ - Fe<br>(FCC) | $2.3 \times 10^{-5}$ | 148                     | 1.53    | 900               | $6.9 \times 10^{-12}$ |
|                        |                      |                         |         | 1100              | $6.3 \times 10^{-11}$ |
| Cu                     | $7.8 \times 10^{-5}$ | 211                     | 2.19    | 500               | $4.2 \times 10^{-19}$ |
| Cu                     | $2.4 \times 10^{-5}$ | 189                     | 1.96    | 500               | $4.0 \times 10^{-18}$ |
| Al                     | $2.3 \times 10^{-4}$ | 144                     | 1.49    | 500               | $4.2 \times 10^{-14}$ |
| Al                     | $6.5 \times 10^{-5}$ | 136                     | 1.41    | 500               | $4.1 \times 10^{-14}$ |
| Al                     | $1.2 \times 10^{-4}$ | 131                     | 1.35    | 500               | $1.9 \times 10^{-13}$ |
| Ni                     | $2.7 \times 10^{-5}$ | 256                     | 2.65    | 500               | $1.3 \times 10^{-22}$ |

Taking natural log on both sides of equation (10), we get

$$\ln D = \ln D_0 - \frac{E_d}{RT} \quad \dots\dots (11)$$

Since  $D$ ,  $D_0$ ,  $E_d$  and  $R$  are constants, it gives a straight line on the graph  $\ln D$  versus  $\frac{1}{T}$ .

$$Y = mx + C$$

$$m = -\frac{E_d}{R} \text{ slope of the y-x graph}$$

$$C = \ln D_0, \text{ y-intercept of y-x graph.}$$

It shows that from  $\ln D$  versus  $\frac{1}{T}$  graph, we can calculate  $D_0$  and  $E_d$ .

The plot of the logarithm of the various diffusion coefficient versus the reciprocal of absolute temperature is given below in figure 5.5.

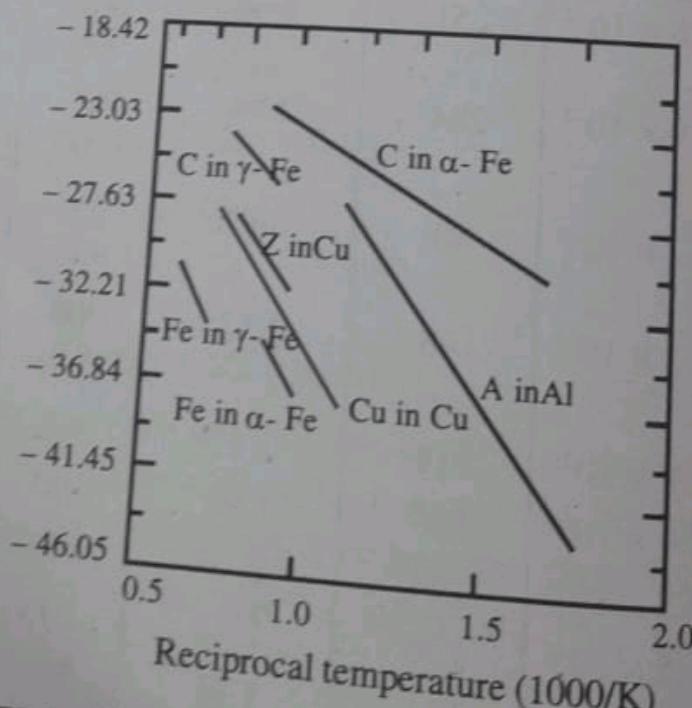


Figure 5.5: Plot of logarithmic diffusion coefficient versus  $\frac{1}{T}$

**Example 5**

Calculate the diffusion coefficient of Zn in Cu at 500°C.

$$D_0 = 2.4 \times 10^{-5} \text{ m}^2 \text{s}^{-1}, E_d = 1.96 \text{ eV/atom}$$

**Solution**

$$\text{We have } D = D_0 e^{\frac{-E_d}{RT}}$$

$$R = 8.62 \times 10^{-5} \text{ eV / atom - K}$$

$$T = 500 + 273 = 773 \text{ K}$$

$$D = 2.4 \times 10^{-5} \text{ } \text{K} e^{\frac{-1.96}{8.62 \times 10^{-5} \times 773}}$$

$$D = 2.4 \times 10^{-5} \times e^{-29.42}$$

$$= 2.4 \times 10^{-5} \times 1.67 \times 10^{-13}$$

$$= 4.0 \times 10^{-18} \text{ m}^2 \text{s}^{-1}.$$

**Example 6**

Compute the diffusion coefficient of carbon in  $\gamma$ -Fe at 900°C.

$$D_0 = 2.3 \times 10^{-5} \text{ m}^2 \text{s}^{-1} \text{ and } E_d = 1.53 \text{ eV / atom.}$$

**Solution**

$$\text{Using } D = D_0 e^{\frac{-E_d}{RT}}$$

$$D = 2.3 \times 10^{-5} \times e^{\frac{-1.53}{8.62 \times 10^{-5} \times 1173}}$$

$$D = 2.3 \times 10^{-5} \times e^{-15.132}.$$

$$D = 2.3 \times 10^{-5} \times 2.68 \times 10^{-7}$$

$$D = 6.16 \times 10^{-12} \text{ m}^2 \text{s}^{-1}.$$

**Example 7**

Calculate the activation energy for the diffusion of copper in gold from the following data

$$D_1 = 3.981 \times 10^{-13} \text{ m}^2 \text{s}^{-1} \text{ at } 1250\text{K}$$

$$D_2 = 3.548 \times 10^{-16} \text{ m}^2 \text{s}^{-1} \text{ at } 909\text{K.}$$

**Solution**

We have

$$D = D_0 e^{\frac{-E_d}{RT}} \quad \dots\dots (1)$$

$$D_1 = D_0 e^{\frac{-E_d}{RT_1}} \quad \dots\dots (1)$$

$$D_2 = D_0 e^{\frac{-E_d}{RT_2}} \quad \dots\dots (2)$$

$\frac{Eq(1)}{Eq(2)}$  gives

$$\frac{D_1}{D_2} = e^{\frac{E_d}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Substituting the values of  $D_1$ ,  $D_2$ ,  $T_1$  and  $T_2$ , we get

$$\frac{3.981 \times 10^{-13}}{3.548 \times 10^{-16}} = e^{\frac{E_d}{R} \left( \frac{1}{1250} - \frac{1}{909} \right)}$$

$$1.122 \times 10^3 = e^{\frac{E_d}{R} \times 3 \times 10^{-4}}$$

Taking natural log on both sides, we get

of copper in

$$\ln(1.122 \times 10^3) = \frac{E_d}{R} \times 3 \times 10^{-4}$$

$$7.023 = \frac{E_d \times 3 \times 10^{-4}}{R}$$

$$E_d = \frac{7.023 \times R}{3 \times 10^{-4}}$$

$$E_d = \frac{7.023 \times 8.62 \times 10^{-5}}{3 \times 10^{-4}}$$

$$E_d = 2.02 \text{ eV/atom.}$$

.... (1)

.... (2)

### Aluminium for integrated circuit interconnects

Here we discuss how does the study of diffusion process in metals enabled us to construct sophisticated integrated circuits which are essential for computers. Integrated circuit (IC) chip is a thin square wafer having dimensions of  $6\text{mm} \times 6\text{mm} \times 4\text{mm}$ . In this millions of interconnected electronic components and circuits are embedded. Usually an IC is made of silicon, to which specific and extremely minute and controlled impurities are added. For some ICs the impurities are added using high temperature diffusion process. To connect the various electronic components IC has to be provided with conducting paths to facilitate the passage of current flow. These paths are called interconnects. To have high electrical conductivity for these paths suitable materials must be chosen. Silver, copper, gold and aluminium are highly conductive materials. On the basis of conductivities silver is the best choice and aluminium is the last choice.

After having done the deposition of interconnects, it is necessary to subject the IC chip to other heat treatments where the temperature goes up to  $500^\circ\text{C}$ . At this temperature silver has significant diffusion

from the interconnects into the silicon, as a result interconnects will be destroyed. To overcome this difficulty we have to select a material which has low diffusion coefficient material in silicon. Among the conductive materials aluminium has least diffusion coefficient. So aluminium is the best material for interconnects.

Copper interconnects are also used to fabricate ICs.

### Diffusion in ionic materials

The diffusion process in ionic materials is more complicated than that for metals. This is because ionic materials contain two types of ions of opposite charge. Both of them will take part in diffusive motion. Usually diffusion in ionic materials occur by vacancy diffusion maintaining charge neutrality. In order to maintain charge neutrality, the following may be said about vacancies. 1) ion vacancies occurring pairs 2) they form in non-stoichiometric compounds and 3) they are created by substitutional impurity ions having different charge states than host ions. The diffusive motion of a single ion is associated with transference of charge. In order to maintain localised charge neutrality in the vicinity of this ion, it is necessary that another species having an equal and opposite charge accompany the ion's diffusive motion. These charged species include another vacancy. As a result of this the rate of diffusion of these pairs is limited by the diffusion rate of the slowest moving species.

When an external electric field is applied across an ionic solid, the charged ions diffuse to the respective polarity of the electric field. This ionic motion gives rise to an electric current.

Since the electrical conductivity is a function of diffusion coefficient, much of the diffusion data for ionic solids come from electrical conductivity of metals.

### Diffusion in polymeric materials

Here our aim is to study the diffusive motion of small foreign molecules such as  $O_2$ ,  $H_2O$ ,  $CO_2$ ,  $CH_4$  methane etc through

polymer. The diffusive motion of chain of atoms within the polymer, of course, take place. A polymers permeability and absorption characteristics relate to the degree to which foreign substances diffuse into the material. This will tend to chemical reactions of polymers and degradation of foreign materials.

The diffusive motion of foreign materials takes place through amorphous as well as crystalline regions. The rate of diffusion is more in the first. This is because amorphous regions are more open. This diffusive motion is considered to be analogous to interstitial diffusions in metals. i.e., in polymers diffusive motion occurs through small voids between polymer chains from one open amorphous region to an adjacent open one.

Two more points to be noted. If the size of the foreign molecule is smaller the diffusion rate is faster. The other is that if the foreign molecules are inert than that react with polymer the diffusion rate is faster.

The diffusion flux ( $J$ ) of gas through a polymeric material having thickness  $\Delta x$ , is directly proportional to the pressure gradient  $\frac{\Delta P}{\Delta x}$ .

$$\text{i.e., } J \propto \frac{\Delta P}{\Delta x}$$

$$\text{or } J = -P_M \frac{\Delta P}{\Delta x} \quad \dots \dots (12)$$

where  $P_M$  is called permecibility coefficient and  $\Delta P$  is the difference in pressure across the polymeric material. This is nothing but the modified form of Fick's first law.

The permeability coefficient  $P_M$  can be approximated as the product of diffusion coefficient ( $D$ ) and the solubility ( $S$ ) of the diffusing species in the polymer. This is valid only for small molecules in nonglassy polymers.

$$\text{i.e., } P_M = DS \quad \dots\dots (13)$$

The unit of  $P_M$  is  $\text{cm}^3\text{STP}/\text{cm}^2\text{sPa}$

This has several applications in everyday life. Polymeric materials are used to food and beverage packing, an to mobile tyres filled with gas, to separate one chemical species from another. Using Fick's law (eq-12) we can calculate the diffusion thereby gives information how long does the diffusing species intact.

For example plastic bottles are used for soda. Soda contains  $\text{CO}_2$  dissolved in water. The  $\text{CO}_2$  molecules slowly diffuse through the polymeric bottle. Using Fick's first law we can calculate how long the bottle can hold  $\text{CO}_2$ . (see example 8).

### Example 8

A soda bottle has a surface area of  $500\text{cm}^2$  and wall thickness of  $0.05\text{cm}$  containing  $750\text{cm}^3$  of  $\text{CO}_2$ . The pressure of  $\text{CO}_2$  inside and outside are  $400\text{kPa}$  and  $0.4\text{kPa}$  respectively.

$$P_M = 0.23 \times 10^{-13} (\text{cm}^3\text{STP})/\text{cm}^2\text{sPa}$$

$$P_1 = 0.4\text{kPa} = 400\text{Pa}$$

$$P_2 = 400\text{kPa} = 400,000\text{ Pa}$$

$$\Delta P = P_1 - P_2 = -399600\text{ Pa}$$

$$\Delta x = 0.05\text{cm}$$

$$P_M = 0.23 \times 10^{-13}$$

$$\text{Using } J = -P_M \frac{\Delta P}{\Delta x}$$

$$J = -0.23 \times 10^{-13} \times \frac{-399600}{0.05}$$

$$= 1.83 \times 10^{-7}$$

The flow

The

Short a

1. W

2. W

3. W

4. W

5. M

6. W

7. W

The flow rate of  $\text{CO}_2$  through the wall of bottle,

$$V_{\text{CO}_2} = JA = 1.83 \times 10^{-7} \times 500 \\ = 9.15 \times 10^{-5} \text{ cm}^3/\text{s}$$

∴ The time taken by  $750\text{cm}^3 \text{CO}_2$  ( $V$ ) through the bottle is

$$t = \frac{V}{V_{\text{CO}_2}} = \frac{750}{9.15 \times 10^{-5}}$$

$$t = \frac{750 \times 10^5}{9.15} = 81.97 \times 10^5 \text{ s}$$

$$t = 2276.94 \text{ hours}$$

$$t = \frac{2276.94}{24} \text{ days}$$

$$t = 94.9$$

$$t = \text{about 3 months.}$$

## UNIVERSITY MODEL QUESTIONS

### Section A

(Answer questions in two or three sentences)

#### Short answer type

1. What is meant by diffusion?
2. What is the cause of diffusion in metals?
3. What is self diffusion?
4. What are the two condition to be satisfied for atomic diffusion ?
5. Mention two models of diffusion type.
6. What is meant by vacancy diffusion?
7. What is interstitial diffusion?